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Ordered Piezoelectric Networks via a Liquid-Crystalline Monomer Strategy:
Synthesis of the LC Monomer

by

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Abstract:

Piezoelectric materials are used in many technological applications. The physical requirements for piezoelectricity are a high degree of bulk order and a noncentrosymmetric bulk structure. Conventional single crystal piezoceramics possess a high degree of order and long term stability; however, they are brittle and difficult to fabricate. Poled piezoelectric polymers offer ease of fabrication and processing; however, they lack long term thermal and mechanical stability. A new technique is described for synthesizing highly ordered, heavily crosslinked piezoelectric networks which offer high order and stability as well as ease of fabrication and processing. Crosslinkable, chiral smectic C liquid-crystalline monomers are used to form a layered noncentrosymmetric phase, which is then oriented by an external electric field to generate a monodomain structure. In situ photopolymerization then forms the final noncentrosymmetric network. The key to the success of this strategy is the design and synthesis of a polymerizable liquid crystal with the correct symmetry and phase properties. In this report, we describe our progress towards such a monomer system.

**Ordered Piezoelectric Networks
Via a Liquid-Crystalline Monomer Strategy:
Synthesis of the LC Monomer.**

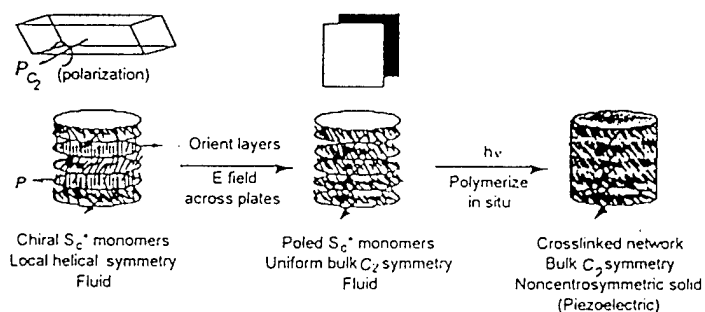
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I Introduction

Piezoelectricity is the interconversion of electrical and mechanical energies.¹ Piezoelectric materials are used in many technical applications such as timing elements, sensors, and speakers. Piezoelectricity arises from materials that are highly ordered and noncentrosymmetric in the solid state.¹ Single crystal ceramics (SCC) (e.g. α -quartz) with noncentrosymmetric unit cells are currently the most widely used materials for piezoelectric applications. The high degree of order of the SCC's enhance their piezoelectric properties; however, SCC's are brittle and thus difficult to fabricate and process.² More recently, piezoelectric polymers formed by poling or doping have become a processable alternative to SCC's, but these materials lack the high degree of order and long term stability of SCC's.²

What we are currently working towards is a highly ordered, piezoelectric polymer network which combines the long term stability and order of SCC's while maintaining the ease of processability and fabrication of conventional polymers. This can be achieved by synthesizing an orientable difunctional monomer which adopts an LC phase with the correct symmetry and polymerizing it to form a highly crosslinked, highly ordered material (Scheme 1). A liquid crystalline (LC) monomer is the ideal candidate for this highly ordered orientable system.



Scheme 1

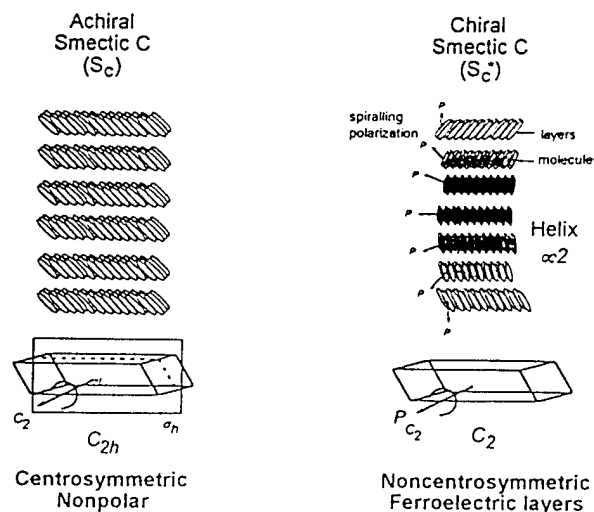
II Experimental Section

The solvents and chemicals were purchased from Aldrich and Fisher Scientific and were used without further purification unless necessary. ^1H - and ^{13}C -NMR spectra were taken on Bruker AMX 300 and 400 machines. Differential scanning calorimetry (DSC) profiles were taken on a Perkin Elmer DSC-7, and polarized light microscope (PLM) pictures were taken on a Leica DMRXP microscope with a Linkam THMSE 600 hotstage. Variable temperature X-ray diffraction was performed using a Inel CPS 120 diffraction system with a programmable capillary oven.

III Results and Discussion

LC's are a mesophase between crystalline solid and isotropic liquid. LC's possess some of the order of solids but the fluidity of liquids.³ We are designing a rod-like thermotropic LC that possesses the chiral smectic C (S_C^*) phase. The smectic C phase has tilted layers and a degree of orientational and positional order.³ Adding a chiral center to each molecule removes the center of symmetry and induces a spontaneous layer polarization (P_S) that can be macroscopically oriented to form a macroscopic

dipole moment in the bulk structure. The C_2 symmetry of the oriented S_C^* phase is such that, when polymerized, the resulting material will be piezoelectric (Scheme 2).



Scheme 2

In designing a S_C^* crosslinkable monomer, it is necessary to determine the structure-property relationships of each portion of the molecule. A schematic representation of a smectic S_C^* LC is shown in Figure 1. A rigid core and flexible tails are generally needed for the smectic phase.⁴ A chiral center yields the S_C^* phase and the polymerizable endgroups are required for crosslinking. The design of LC's is mostly an empirical process; one cannot predetermine that a particular molecule will be necessarily LC.⁵ To date, no one has combined all of these qualities into a single LC molecule.

Requirements for an S_C^* Monomer

1. Rigid core \Rightarrow for S_C phase
2. Flexible hydrocarbon tails \Rightarrow for S_C phase
3. Chiral center \Rightarrow for S_C^* phase
4. Polymerizable end groups \Rightarrow for polymerization

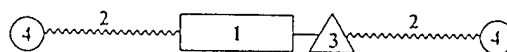
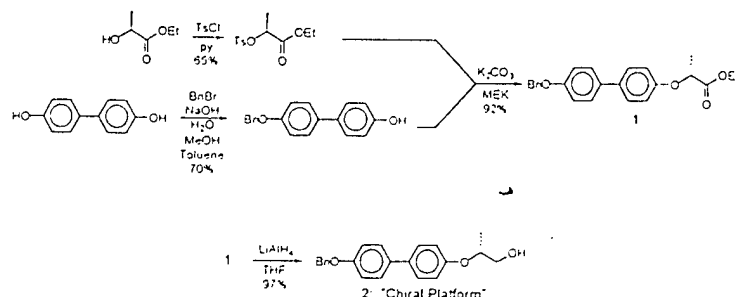
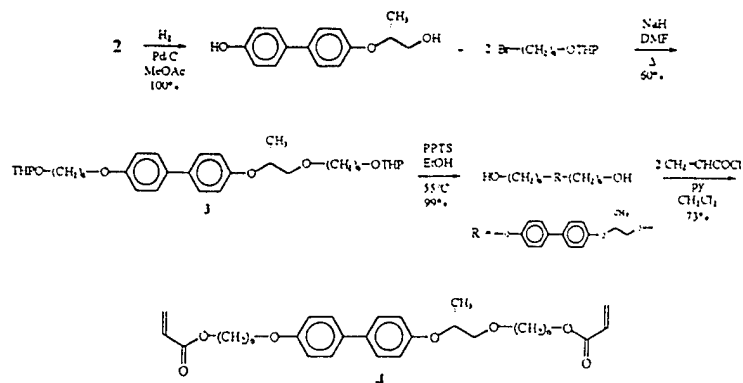


Figure 1

Using known LC's as a design guide,^{4,6,7} the design of an original S_C^* monomer was initiated. Previous S_C LC's have incorporated a biphenyl core.⁴ Previous S_C^* LC's incorporated a chiral center derived from (+)-ethyl lactate,⁸ an inexpensive commercial source of an optically active material. Terminal acrylates have been shown to not substantially affect the phase behavior of a particular mesogen.⁹ The synthesis is shown in Scheme 3. In the event that a modification needed to be made to our molecule to make it S_C^* , our molecule had to be modular in its construction. Also, since this must be an industrially viable material, the starting materials needed to be inexpensive and the chemical reactions facile.



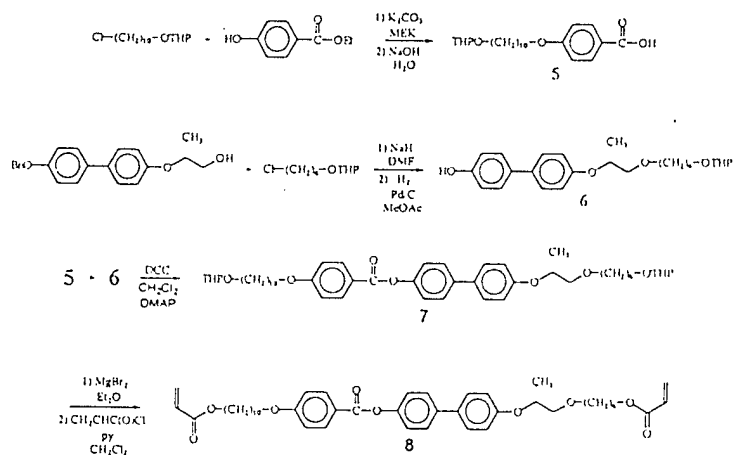


Scheme 3

The first step was to form a central core from which the rest of the molecule could be built. Biphenyl was chosen as the rigid core and a chiral center was placed adjacent to the biphenyl unit. The resulting "chiral platform" is depicted as molecule 2. From this platform, the benzyl group was removed via catalytic hydrogenation and hexyl hydrocarbon tails were placed on both sides of the molecule to form 3. The tetrahydropyranyl (THP) groups were removed with PPTS in EtOH and the acrylate groups were introduced to form monomer 4.

^1H - and ^{13}C -NMR spectroscopy showed this molecule to be of high purity. The substance was a viscous oil. Polarized light microscopy measurements, however, failed to provide any proof of an LC phase. Crystallization could not be induced at ambient or subambient temperatures, so the hopes for a thermotropic LC with a transition to the LC phase at an elevated temperature would have to be found in a revised molecule.

Returning to the literature, we found that a molecule with at least one more phenyl group and some form of lateral dipole moment (i.e. an ester linkage) seemed to induce the S_C phase.¹⁰ The synthesis of a revised monomer is shown in Scheme 4.



Scheme 4

The chiral platform 2 was taken and a THP-protected 6-bromohexanol was added via an ether linkage. The benzyl group was removed and the addition of fragment 5 via a DCC coupling nearly completed the new target. Removal of the THP groups and introduction of the acrylates would get us to the revised monomer 8.

DSC scans have been taken of all of the molecules up to the di-THP compound 7. Some of the intermediate materials, such as 5, exhibited LC character, which was confirmed by PLM. The latest molecule to be synthesized, 7, was shown to be LC by DSC (Figure 2). Compound 7 appeared to contain a chiral nematic phase as well an S_C phase. The

confirmation of these LC phases is currently being performed using variable temperature low-angle X-ray diffraction.

IV Summary

LC monomers will be polymerized to form a rigid piezoelectric network. The structural morphology has been studied extensively in the attempt to predict a crosslinkable monomer that will be S_C^* . This has proven to be difficult, but progress is still being made. At the very least, this chiral monomer has the approximate shape of a similar achiral LC S_C monomer. In this case, the non-LC chiral monomer can be combined with a S_C matrix monomer with retention of the original S_C phase. This resulting mixture can then be polymerized to yield a noncentrosymmetric network with piezoelectric properties.

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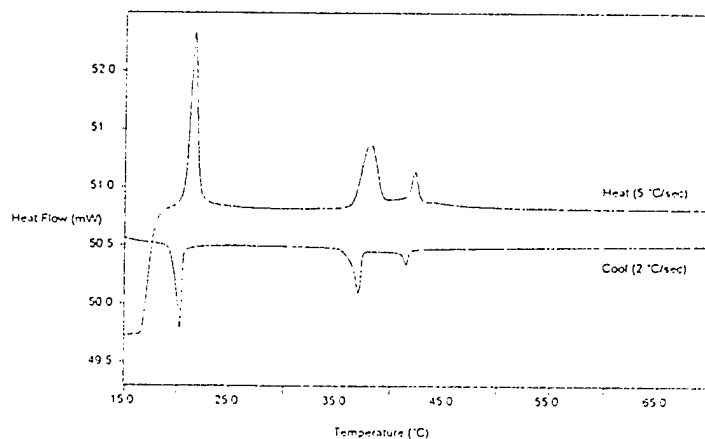


Figure 2